

# The Dembovsky's theory of glass formation

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In this memory paper the scientific way of Prof. Dembovsky (1932-2010) is presented. It can be divided into four successive steps: (1) investigation of *materials* belonging to chalcogenide glass-forming compositions; (2) construction of *empirical theory of glass formation*; (3) introduction of "*quasimolecular defects*" (QMD) as microscopic basis of the glassy state, and (4) transformation of QMD into *hypervalent bonding configurations* (HVC), which are not "defects" but a necessary component of glass structure and a general cause of glass formation and glass specificity; the existence of HVC in glasses being justified by direct quantum-chemical calculations. As a result, Dembovsky have created a principally new basis for understanding of glass nature, an approach that merits an appropriate recognition and further development.

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## 1. Introduction

The first paper of Sergei Aristarkhovich Dembovsky (Dembovskii) was appeared in 1958, two years after his graduation from Chemistry department of Moscow State University. This article, concerning chemistry of ocean water, was a result of his work on the board of *Vityaz*, the Russian scientific ship. The second article of Dembovsky, as well as all others (almost 200), were devoted to glass, his lovelies object for preparation, experimenting and theorizing. For half a century, from 1959 to 2010, glass was the first (though not a single) thing in his life. In this paper I consider four rather sharp periods of his "love story" with glass, three of which I can see directly since enter in his group in 1980.

The first period (1959-1976) was a time of intensive and often pioneering *investigation* of numerous chalcogenide systems in which glass formation can be observed: their phase diagrams, glass-forming regions, crystallization ability and features, together with various properties (mechanical, optical, electric, structure, ESR, NMR, etc.) of glassy and crystalline phases. This work was tightly connected with practice: from laboratory preparation to industrial production, from specific composition/properties to their application in devices that use chalcogenide glasses as a new class of materials – *glassy semiconductors*.

Experimental information obtained by Dembovsky has achieved a "critical mass" at about 1975, when he began to summarize and analyze his experimental results as a whole. At 1977 he published the *Empirical Theory of Glass Formation*, which relates few basic characteristics of a substance in the form that permits to predict its glass-forming ability, firstly in a semi-quantitative manner form

and some later even in quantitative form of critical cooling rate. It was a really an outstanding result, that has no an analogue up to now. Nevertheless, for Dembovsky it was only the first step, in which he reveals the electronic-coordination relation in the form of optimum-high concentration of lone-pair electrons  $\Psi=0.5-0.66$ , which is typical for glass-forming substances.

The sense  $\Psi$ -criterion was understood at early 1980s, when it became possible to connect glass-forming ability with participation of lone-pair electrons in formation of specific electron-rich bonds. This step means a transition from ideal glass in its classical form of continuous random network to a real glass having an additional degree of freedom due to the chemical bond option. The name of alternative bond was evaluated from *quasimolecular defect* (QMD) through *three-centre bond* (TCB) to *hypervalent configuration* (HVC), which is the most general term. The nature of this bond was investigated in several ways: (1) by examination of the glass-crystal difference in various properties, as it can be caused by HVC, (2) by special experiments, which may reveal HVC as such, (3) by quantum-chemical calculation of HVC in various glass-forming substances. Dembovsky explored also interdisciplinary approaches, such as information indices, chirality, symmetry, in order to understand in what a way HVCs interact with "normal" bonds resulting in a specific state of matter – the glassy state.

Dembovsky was forced to hamper his outstanding scientific activity after the stroke at 26 February 2000. However, up to his death at 26 November 2010 he has used all possibilities to preserve and develop his approach. Thus, the primary goal of this paper is to present the Dembovsky's scientific way in hope that his ideas will revives in the proceedings of young scientists who are

fascinated with an old puzzle of the glassy state, as he was. Another aim, of course, is to honor Sergei Dembovsky together with his old friends and colleagues at this Conference, the first international conference on chalcogenide glasses after his decease.

## 2. Step 1: Chalcogenide glasses - materials research

Since 1962 to 1976, i.e. for 15 years only, Dembovsky has published almost 90 articles concerning preparation and investigation of numerous chalcogenide glass-forming systems belonging to a newly specified perspective class of materials - glassy semiconductors. There is no one scientist, I think, who made so an intensive and large contribution in this field of material science.

Dembovsky began from As-Se system, where he suspected a new compound, AsSe [1], which he justified some later [2]. Soon the full phase diagram of this now classical system was obtained [3]. The following two-component systems were: Ge-Se [4], As-S [5], As-Te [6], P-Se [7]. Then composition becomes more complex: Dembovsky and his group investigate three-component systems, first of all As-Se-Ge [8], As-Se-Te [9], Ge-As-S [10], As-Se-S [11], As-Ge-Te [12] (for each system only one article is cited as an example). Two series were investigated most intensively: the systems with thallium (22 articles, e.g., [13]), and those with iodine (20 articles, e.g., [14]). The elements from all Groups of Periodic Table, except VIII group of inert gases, were added to chalcogenides (VI): Cu, Ag (I); Cd, Hg (II); B, Tl (III); Si, Ge, Sn, Pb, Ti (IV); P, As, Sb, Bi (V); Br, I (VII). The system complexity varied from one-component (Se) to four-component.

During investigation the first aim was to construct phase diagram of the system (by thermal treatments and DTA analysis, first of all), the second aim – to evaluate its glass-forming region and/or crystallization fields, and finally – to investigate various properties as a function of both glass composition and in comparison with related crystals. The properties investigated were IR-spectra, viscosity, ultrasound velocity, microhardness, microstructure (including electron microscopy), X-ray, ESR (with  $Mn^{2+}$ ,  $Gd^{3+}$ , and  $Fe^{3+}$  additions), NMR, thermo-electric and photo-electric features, and so on. It is essential that not only glass-forming composition with the desired properties, but also the general trends in changing of structure and properties when changing chemical composition were searched systematically. Correspondingly, there are two main results of this period. First, the data were involved into information base on chalcogenide systems as an actually impersonal knowledge. Second, owing to such a wide and intensive investigations of material in both glassy and crystalline state, Dembovsky was perfectly armed when he naturally came up to the key problem of glass formation: what is the reason that permits some substances to form bulk glass when slow cooling from melt, while other substances

(even belonging to the same system) need rapid cooling, or film/span technologies, or cannot exist in solid amorphous state at all.

## 3. Step 2: Empiric theory of glass formation

The 15-year experimental work creates the Dembovsky's feeling of *glass-forming ability* (GFA) as a function of few fundamental parameters. To specify this feeling the primary goal was to identify these parameters and to find an appropriate form of their relation. His first work on "empiric theory of glass formation" [15] Dembovsky begins from electron analogues (iso-electronic rows), the substances with equal number of valence electrons per atom. The idea was to compare *concentration of valence electron* per atom (VEC) with the *complexity* of a system (elements, more or less complex compounds), on the one hand, and with their ability for glass formation, on the other hand. The resulting table demonstrate a step-like form with raptures at  $VEC < 4$  and  $VEC > 6$ . Then  $K$ , the average atomic *coordination in melt* (since glass structure is nearer to melt than to crystal) was introduced. The combined value  $\Delta = (VEC - K)$  was successively related with the known GFA for simple elements (S, Se, Te) and binary compounds ( $As_2S_3$ ,  $As_2Se_3$ ,  $As_2Te_3$ ). When adding the abovementioned complexity in the form (A+E), where A is the number of one-sort atoms and E is the number of structural units or phases (namely,  $E=1$  for element or compound, and  $E=2$  for intermediate compositions), Dembovsky have written his first equation for GFA in the form of

$$C = [(A+E)/2] * \Delta = [(A+E)/2] * (VEC - K) \quad (1)$$

where C is a non-dimensional measure of GFA ("C" is the first letter of "glass" in Russian). Note that  $[(A+E)/2]$  is a twice reduced value of initial complexity (A+E), so that the simplest case of element (Se, etc.) corresponds to  $[(A+E)/2]=1$ .

This equation occurred to be suitable for not only elements and compounds but also for calculation of glass-forming region in a binary system, as it was firstly demonstrated in 1977 [15] using Se-Ge as an example. "Good glasses" (those that can be prepared as bulk, so using a relatively slow cooling of melt) corresponds to  $C > 4$ ; the higher C the better GFA (the critical cooling rate decreases), and *vice versa*. Thus, for the first time not only calculation of glass-forming region but also the region dependence on the regime of cooling were achieved.

As Dembovsky emphasized, the physical sense of eq.(1) is close to the sense of classical "phase rule": really, there is a few interconnected parameters (VEC, K, E, A) that can be changed only in definite limits, when changing chemical composition, for glassy state to persist.

All the parameters are known from composition and the phase diagram of the considered system (Se-As, etc.), with a possible exception of K as far as coordination in melt is often unknown. But in this case one can solve the reverse problem: by using eq.(1) and known C (from known GFA) to calculate the K value. In such a way the *compulsive coordination effect* in telluride glasses was described by Dembovsky in 1978 [16]. This effect (that is observed also in other chalcogenide and even oxide glasses) means that the element (Te, etc.) when introducing into glassy matrix changes its coordination depending on the matrix, e.g., Z(Te)=4 in the systems Te-In and Te-Ge, and Z(Te)=6 in Te-As<sub>2</sub>Te<sub>3</sub>-As and Te-As<sub>2</sub>Se<sub>3</sub>.

Later some imperfections were introduced into the calculation procedure of GFA. The first one [17] takes into account *liquidus temperature* (in the form of coefficient  $\gamma = \Sigma(T_i * N_i) / T_L$ , where  $\Sigma(T_i * N_i)$  is *interpolated* melting temperature between particular points in phase diagram for the given composition N<sub>i</sub>, and T<sub>L</sub> is a *real* liquidus temperature from the known phase diagram of the system under consideration. Then [18] the procedure of interpolation was strictly determined, including taking into account metastable phase diagram, as it is shown in Fig.1.

In order to come up nearer to basis of glass formation, the non-dimensional value C was transformed into energetic barrier for crystallization [20]

$$\Delta E_{cr} = (E_d / VEC) * C = E_d * [(A+E)/2] * [(VEC-K)/VEC] = E_d * [(A+E)/2] * \Psi \quad (2)$$

where E<sub>d</sub> is the average energy of bond breaking or bond dissociation, which is calculated from atomization energy for elements and compounds (known thermodynamic data). Since ΔE<sub>cr</sub> is an essentially artificial value, just because of a simple multiplication-division (better-worse) method that was used in eqs.(1,2), there needs a translation between calculated values of C and ΔE<sub>cr</sub> and a real energetic barrier, on the one hand, and between this barrier and critical cooling rate (CCR), on the other hand. These problems were solved in our following papers [21], in which ΔE<sub>cr</sub> was related to G<sup>#</sup>, the *barrier of initial reorientation*, and G<sup>#</sup> gives the value of CCR when *characteristic frequency* ν<sub>0</sub> (lgν<sub>0</sub>[Hz]=11 for chalcogenide glasses) is known.

The method for calculation of CCR was successively used also for amorphous metals [22] and oxide glasses [23]. By my opinion, this calculation approach can be developed further, particularly for understanding of the nature of *initial reorientation* and its characteristic frequency. Dembovsky, however, has gone further, continuing his search of a general reason for glass formation.

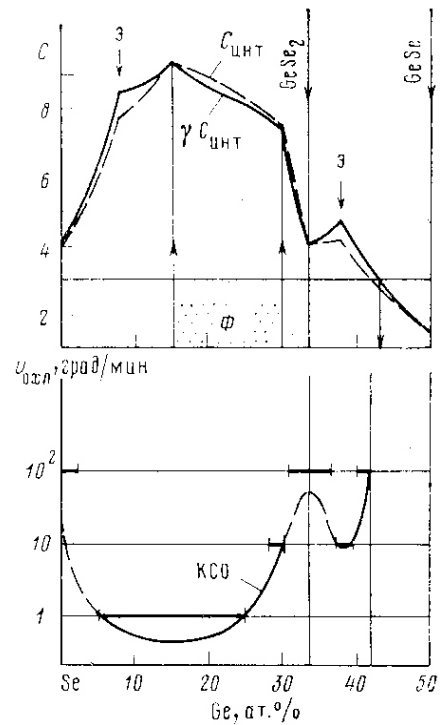


Fig.1. Calculated glass-forming ability in the form of C after [18] (at the top) in relation with semi-quantitative data for critical cooling rate and the region of metastable Φ-phase after Azouley et al. [19] (at the bottom). This picture is from ref.18.

#### 4. Step 3: Ψ-scale and quasimolecular defects (QMD)

Just in his first theoretical paper in 1977 [15] Dembovsky has emphasized the role of lone-pair electrons in glass formation by means of introduction of criterion Ψ=0.50-0.66. Here Ψ=(VEC-K)/VEC represents the number of electrons, which are disposed on the outer shell but not participate in chemical bonding, divided by the total number of outer electrons, i.e. concentration of the so called "lone-pair" (LP) electrons. Remember that K means coordination, i.e. the number of existing bonds per atom, then (VEC-R) is the number of electrons that are "free" of chemical bonding. Note that is one of three general constituents of eq.(2) describing glass forming ability.

The case of Ψ=0 means that atom realize all his bonding ability due to its outer shell (VEC=K), thus reaching maximum valence when connecting with its neighbors. Glass-forming elements Se and S from VI group have s<sup>2</sup>p<sup>4</sup> outer electronic configuration and K=2 (each atom is two-coordinated in chains and/or rings in all states: crystal, melt, glass), hence Ψ=(6-2)/6=0,66. Their electronic analogue Te, however, cannot form bulk glass because increases its coordination when melting up to K=6, thus using all its outer electrons (Ψ→0). Similar calculations can be made for every element and compound, despite of character of bonding and glass-forming ability. In this way one obtains Ψ-scale like that shown in Fig. 2 (the first variant of this scale was published by Dembovsky at 1978 [16]).

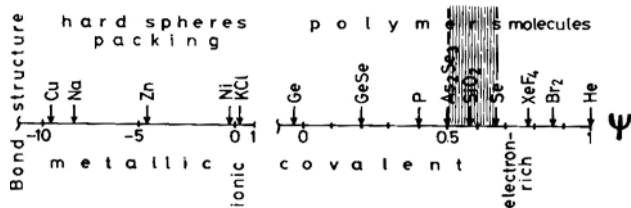


Fig. 2.  $\Psi$ -scale (see text for details) with the shaded region for glasses. This picture is from ref.24.

The principal question of what means the limits  $\Psi=0.50-0.66$  was firstly considered by Dembovsky from stereochemistry point of view, based on the known effect of lone-pairs on structure due to their electrostatic repulsion. This approach, both in its "ordering" variant when LPs locates at definite ends of coordination polyhedra, and in its "disordering" variant (loosening structure, free volume, etc.), occurred to be of low efficiency. Fortunately, in 1980 there appears a model of *quasimolecular defect* (QMD) in amorphous selenium, which was proposed by Popov [25] as an alternative for VAP, famous *valence alternation pair* after Kastner, Adler and Fritzsche [26]. The Popov's model, shown at the top of Fig.3, imitates the molecular-orbital picture of the so called electron-rich (orbital-deficient) molecules of halides ( $I_3^-$ ,  $XeF_4$ , etc.). In the case of continuous random network of glass such *three-centre four-electron* bonds (TCB) are imbedded into the network, so they are not isolated molecules but "quasimolecules", being linked with "normal" two-centre two-electron covalent bonds. Thus there appears a simple explanation for the upper limit of glass region in  $\Psi$ -scale: when LP-electron concentration is too high ( $\Psi>0.66$ ) covalent network becomes unstable due to the LP repulsion. The lower limit ( $\Psi<0.50$ ) probably means that covalent network is extremely stable against formation of TCBs since concentration of LP-electrons is too small for providing enough free volume for existence of relatively weak and long TCB there.

A principal step made by Dembovsky was his statement that QMD is not only alternative to VAP but also – and first of all – QMD is much more than a defect. In 1981, immediately after Popov [25] Dembovsky has published his ground work "The connection of quasidefects with glass formation in the substances with high lone-pair electron concentration" [28], in which he relates this microscopic object with macroscopic phenomenon – high viscosity of for glass-forming liquids. When melting, crystal of glass-forming substance can avoid high-temperature rapture of covalent bonds by transforming them into QMDs, which link fragments of covalent network, thus remaining "continuous" or "polymeric" structure of a relatively high viscosity. Such a network readily forms supercooled liquid and then solid glass when further cooling. Of course, "polymerization ability" of QMD depends not only on the substance but also on temperature; at boiling point the network destroys all the same. Then in glass-forming liquids average coordination may vary in wide limits, including sub-coordinates and super-coordinated cases. The latter was of

especially interesting for Dembovsky, who presented and emphasized the experimental facts that first coordination number of glass-forming liquid can be even *increased* in comparison with related crystal [28], a property that cannot be understood in the limits of classical continuous random network, even when CRN contains the so called "wrong bonds" or VAP.

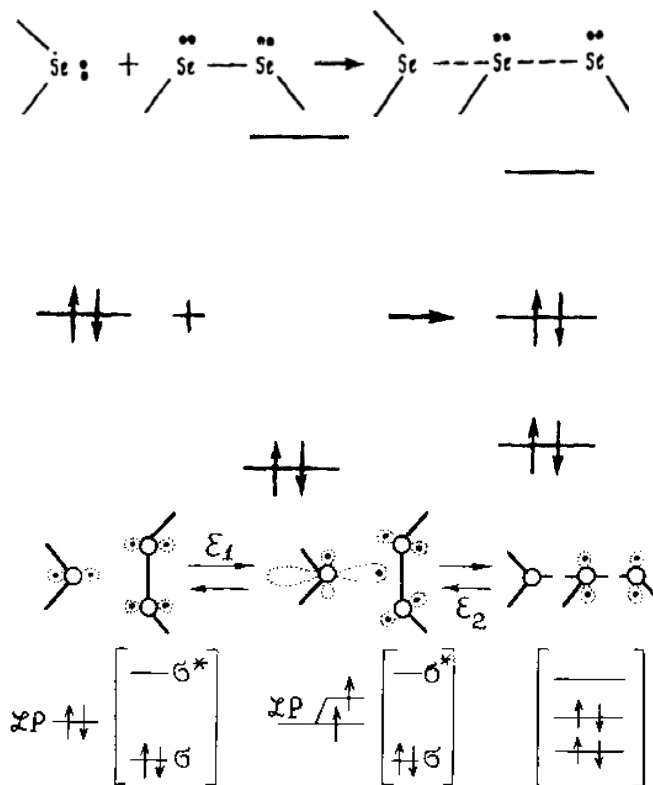


Fig.3. Formation of quasimolecular defect in Se after Popov [25] and its transitional state after Dembovsky & Chechetkina [27].

Being focused on viscosity as the key property for glass formation, Dembovsky began experimental search of QMD in special experiments of viscous flow in magnetic fields, both constant [29] and alternating [30]. The effect was especially interesting in latter case shown in Fig. 4.

Generally speaking, employing of *magnetic* field was a rather strange idea, since both covalent bond (CB) and three-centre bond (TCB) are diamagnetic, as well as VAP. On the other hand, viscosity is a *process* of atomic rearrangement that may proceed by means of *switching* of covalent bonds between atoms (switching is less expensive than breaking of bonds). Many-center bond like TCB is a fine promoter of covalent bond switching, and magnetic field can effect on the switching direction, and hence on viscosity, when transitional state (TCB)\* is paramagnetic. A possible model for such a state is given in the bottom of fig.3, where two-coordinated atom (CB) is linking to one or another neighbor chain by initial one-electron excitation of lone-pair (electronic "harpoon" for adjacent chain), with the following TCB formation:  $CB \rightarrow (TCB)^* \rightarrow TCB$ .

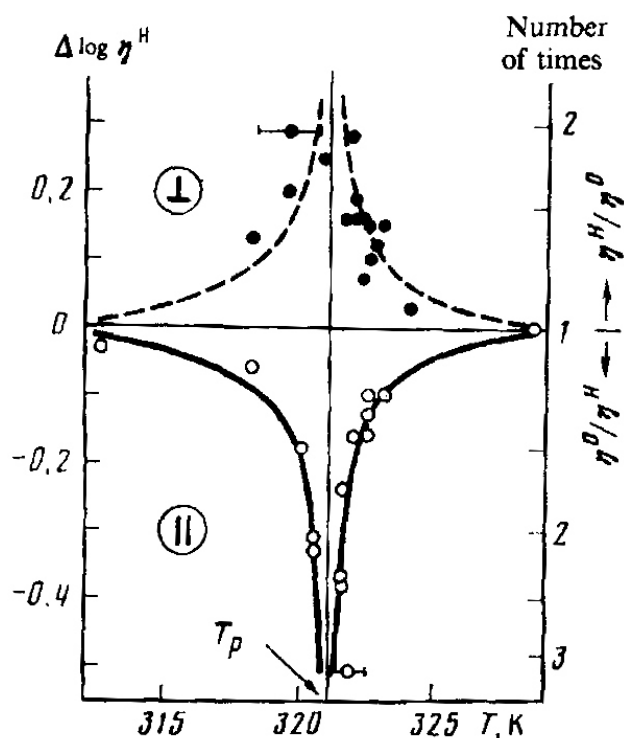


Fig.4. Effect of alternating magnetic field (50 Hz, 200 Oe) on viscosity of Se [30]. Symbols in circles denote the direction of the field relatively to the flow direction.

This key experiment has two features: orientation and resonance. Orientation reveals itself in the fact that viscosity increases when field direction coincides with the viscous flow direction, i.e. in “parallel” magnetic field, and decreases in “perpendicular” field. Note that magnetic field of  $H=200$  Oe is very *weak*, being of the order of Earth magnetism. Therefore field unlikely creates paramagnetic “harpoon” (this is an equilibrium temperature activated process) but likely increases *probability* for “harpoon” to born and/or to link in the field direction.

Resonance reveals in a dramatic increase of the effect at a definite *temperature* of the sample (321K). The observed resonance likely takes place when the field *frequency* (50 Hz) coincides with the temperature-dependent frequency of some internal process. It is naturally to relate this process with bond exchange ( $CB \leftrightarrow TCB$ ), and the frequency with periodic thermally activated jumps  $CB \rightarrow TCB \rightarrow CB$ , etc. Based on this idea we elaborated a special model by which TCB concentration (actually, a relative number of atoms participating in TCB) was estimated to be 30% at boiling temperature (880K) and 10% at melting temperature ( $T_m=494K$ ) [31]. Thus, if one considers TCB as a defect – it is a low-energy defect (0,14 eV after [31]) with a rather high concentration, even in glassy state. The fact that glass structure imitates the structure of supercooled liquid means the existence of over-equilibrium TCB in solid glass, both in the form of real bonds and in the form of corresponding “voids” in the structure.

Existence of hyper-coordinated soft TCB in a rigid covalent network open new possibilities for interpretation of various effects in glasses, from “micro” (e.g. photo-ESR and photo-luminescence [31]) to “macro” (e.g. photostructural changes [31]); various features and their theoretical description, e.g., low-temperature anomalies and two-level potentials [27], pinning of Fermi level [32], jumps of heat capacity at glass transition in “strong” and “fragile liquids” [33], light-induced gyrotropy and anisotropy [34,35], residual (zero) entropy in glass [36], and so on. The reader can find the detailed interpretations of these and other properties/notions in the cited articles and in reviews [23,37,38]. Nevertheless, in spite of the Dembovsky's numerous publications and scientific contacts, TCB does not spread actually into external scientific medium. There may be various reasons for this, including the healthy skepticism, which arises when one proposes a relatively simple basis for so a complex and puzzle object like glass. While Dembovsky saw only TCB as such a basis, the others even disbelieved in TCB existence. Thus the following step made by Dembovsky was to demonstrate an existence of TCB in glass in a more direct way.

#### 5. Step 4: Hypervalent configurations (HVC) in glasses

The quantum-chemistry group of Dembovsky, leading by A.S. Zyubin, began in 1984 with the simplest case of sulfur using semi-empirical MNDO level; really, a number of metastable TCB was obtained there [39]. In the following works it was revealed, however, that in glass formers TCB is likely exclusion than a rule, the more general case being *hypervalent configurations* (HVC), and TCB being a particular case of HVC. Nevertheless, the explored earlier principal features of TCB, such as soft two-well potential and low-energy over-coordinated bonding state, not only remained but acquired a concrete and numerical form. For example, in **fig.5** one can see the formation of *four-coordinated* HVC in Se (a state that is not considered in initial model in fig.3, where only tree-coordinates Se atoms are present). In fact, this is the situation proposed by the authors of VAP [26] as the way for obtaining of the lowest-energy defect, intimated VAP (IVAP). Calculation chemistry, however, gives an opposite result, just beginning from the demand to VAP to be the *charged diamagnetic* defect. Really, it is seen in fig.5 that in its ground state VAP is neutral but paramagnetic ( $Se_3^0 + Se_1^0$ ). Moreover, when intimation of VAP components IVAP does not realized (because there is no a well in the potential curve), and the process leads to HVC in the form of  $Se_4^0$ , which is *neutral and diamagnetic*, possesses asymmetrical *two-well potential* (there is only the scheme in the top of fig.5, and actually there are two pairs of bonds around central atom, one pair shorter than another pair) and a relatively *low energy* of the ground state, approximately 0,7-0,8 eV.

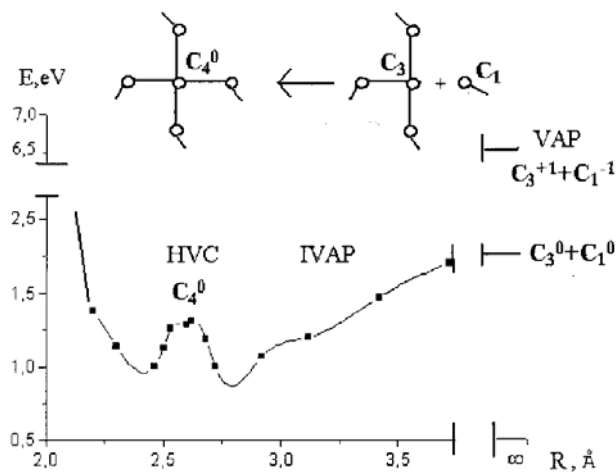


Fig.5. Formation of HVC in selenium in the process of modeling of IVAP formation. This picture is from ref. 40 (C denotes chalcogene atom, here Se, index above is charge, index below is coordination).

In other glass formers (S,  $\text{As}_2\text{S}_3$ , etc., as well as in classical oxide and halide glasses which were calculated – see review of results up to 2000 in ref.37) the picture was principally the same: there were no VAP/IVAP but various HVC can exist, the HVC formation being facilitating as far as more refined methods of calculation were used (from MNDO to *ab initio* calculations with the account of electron correlation effects). Not only structure/geometry and energy of HVC was modeled, but also various properties (optical, electronic) and processes (bonds deformation and switching) are considered – see e.g. refs.41,42.

After 2000 selenium was the main object that we used for checkout of the calculation scheme, on the one hand, and for researching the effect of impurity (Te, Cl, As, Ge, Cl) and/or of HVC aggregation [43-45], on the other hand. The most interesting results of last years are shown in Fig. 6.

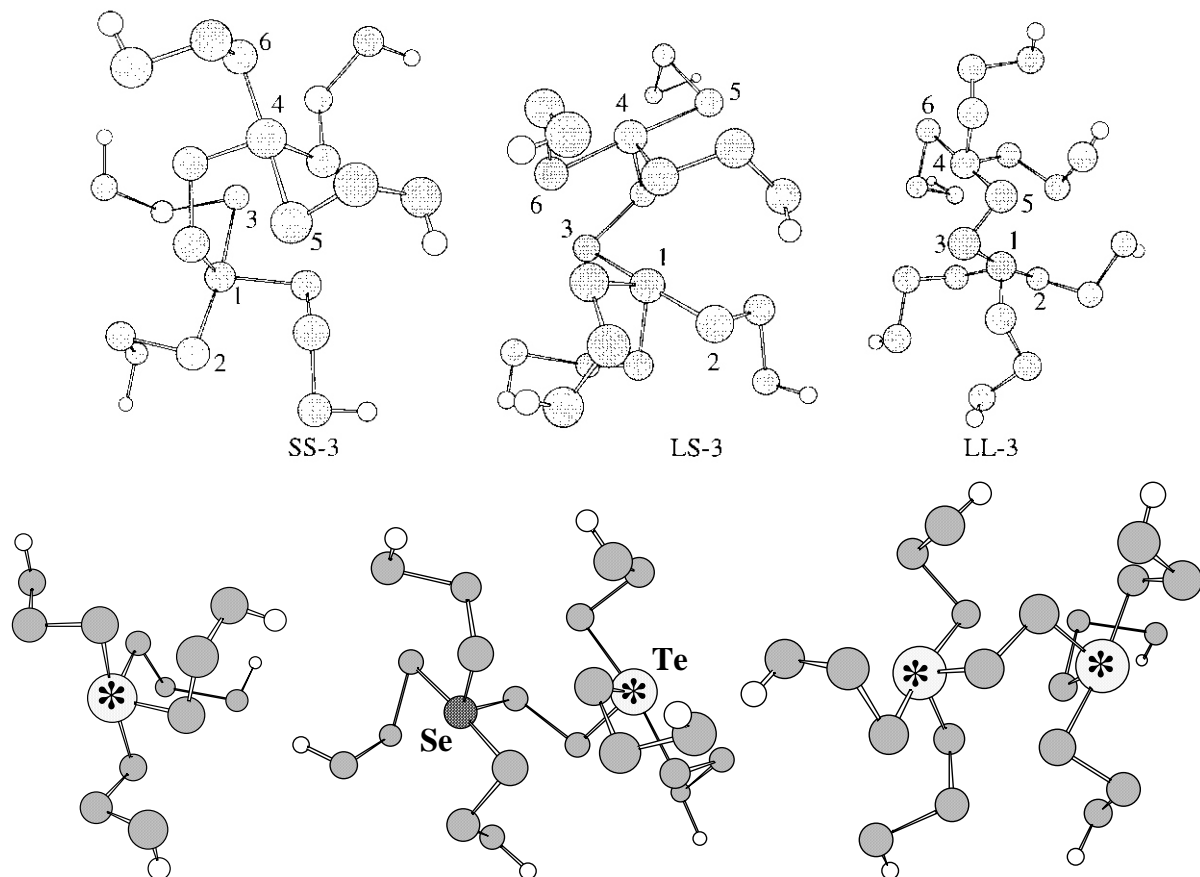


Fig.6. Quantum-chemical modeling of aggregated HVC in Se [43] (upper line), and in Se with addition of Te [45] (lower line). The symbols SS, LS and LL means mutual orientation of HVC as related to short (S) and long (L) pairs of bonds belonging to the  $\text{C}_4^0$  atom.

The first attempt to consider collective HVC by intimating of two  $\text{Se}_4^0$  gives an interesting result: while single  $\text{Se}_4^0$  has the energy of  $E=0.30$  eV relatively to the energy of surrounding continuous random network (CRN

is imitated by cluster of disordered chains, each terminated to H-atoms to avoid influence of boundaries), two  $\text{Se}_4^0$  in neighbor chains decrease the energy of their local region, up to *negative* values. For three upper configurations

shown in fig.6 there are  $E(SS)=-0.16$  eV [!],  $E(LS)=0.08$  eV and  $E(LL)=0.09$  eV [45]. Introduction of Cl, which is known as non-glassforming agent for Se, unexpectedly *decreases* the energy of local region containing HVC: up to  $E=-0.57$  eV for a particular configuration shown in Fig.3 of ref.44. And a really gigantic decrease of energy was observed when Te is incorporated into selenium network, from  $E=-0.23$  eV for single  $Te_4^0$ , through  $E=-0.65$  eV for  $(Se_4^0/Te_4^0)$ , up to  $E=-1.19$  eV for the SS configuration of two  $Te_4^0$  in the lower line in Fig.6.

From these calculations it follows that HVC are inclined to aggregation, a fact that leads directly to the problem of ordering in glasses (anisotropy, clustering, medium-range order), which are the subject of permanent discussion. Note, that in many works (e.g. [23,24,32-38]) Dembovsky connected the above forms of ordering just with collective/aggregated HVCs, which are justified now by means quantum chemistry.

## 6. Concluding remarks

Thus at the end of XX century, which coincided with the last years of his scientific activity, Dembovsky was successively developed his approach, and not only from "chemical" point of view, by also by means of "physical" and interdisciplinary approaches, such as theory of information and symmetry [46], symmetry and order-disorder [47], self-organization [48], phase transitions [49]. Unfortunately, the further development in these directions was interrupted by his disease. Nevertheless, Dembovsky was published in 2007 his last paper, in which made the next attempt to support the idea of HVC as the basis of glassy state [50]. Now it is time for young scientists to test and use his ideas and methods; to know them, for the beginning.

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